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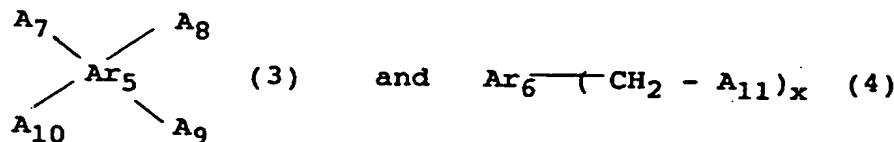
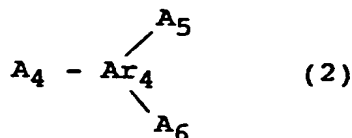
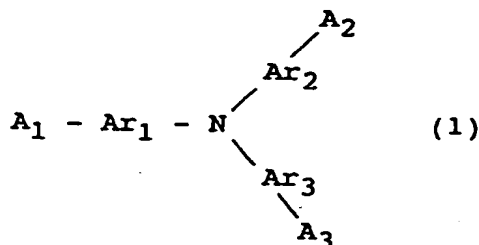
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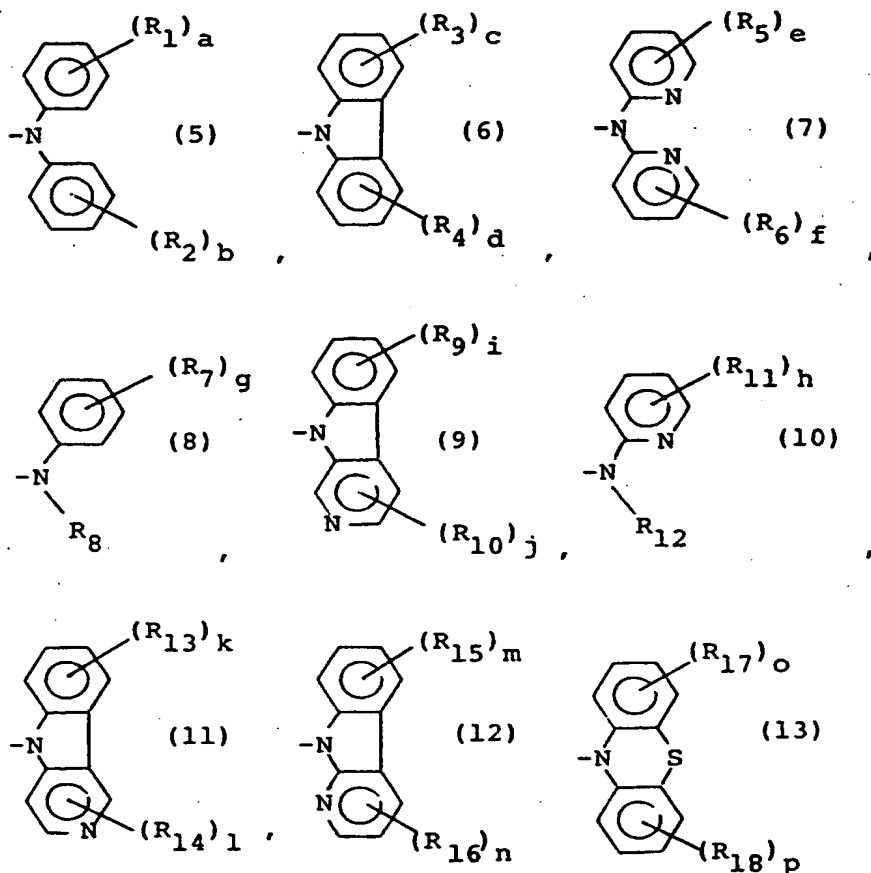
(54) **Organic electroluminescence devices.**

(57) An organic electroluminescence device comprising: a luminous layer containing a luminous material and a hole transport material, or a luminous layer containing a luminous material and a hole transport layer containing a hole transport material, between a pair of electrodes at least one of which is transparent or translucent, characterized in that the hole transport material contains an aromatic amine selected from the group consisting of compounds represented by the formulae (1) to (4)



wherein each of Ar₁, Ar₂, Ar₃, Ar₄, Ar₅ and Ar₆ independently represents an aromatic hydrocarbon ring group having six or more carbon atoms or an aromatically heterocyclic compound group having four or more carbon atoms, x represents an integer of 2 or more, and each of A₁, A₂, A₃, A₄, A₅, A₆, A₇, A₈, A₉, A₁₀ and A₁₁ independently represents a group selected from the following formulae (5) to (13) (plural A₁₁s may be the same or different);

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wherein each of R_1 to R_7 , R_9 to R_{11} and R_{13} to R_{18} independently represents a member selected from the group consisting of C_1 - C_{12} alkyl and alkoxy groups, C_6 - C_{14} aryl and aryloxy groups, a nitro group and heterocyclic compound groups; when one benzene ring or pyridine ring has plural substituents, they are selected independently; each of R_8 and R_{12} independently represents a member selected from the group consisting of a hydrogen atom and C_1 - C_{12} alkyl groups; and $a, b, c, d, e, f, g, h, i, j, k, l, m, n, o$ and p represent integers of $0 \leq a, b, g \leq 5$, $0 \leq c, d, e, f, h, i, k, m, o, p \leq 4$ and $0 \leq j, l, n \leq 3$.

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to an organic electroluminescence device (hereinafter referred to as organic EL device), and more particularly to an organic EL device with a particular aromatic amine compound as hole transport material.

Description of Related Art

Hitherto, inorganic electroluminescence devices are used, for example, in flat light sources as back light, display devices (e.g. flat panel display) and the like. However, AC source of high-voltage is necessary for emission of light from the devices.

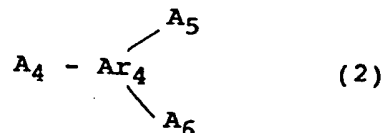
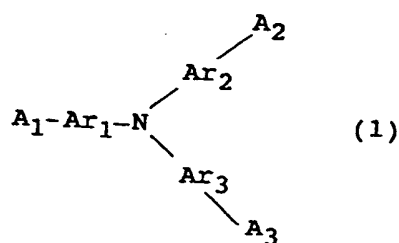
Recently, C.W. Tang et al. produced an organic EL device of two-layer structure composed of a luminous layer comprising an organic fluorescent dye and a hole transport layer, laid on the former layer, comprising a triphenylamine derivative to realize an organic EL device driven by DC source of low-voltage and having high efficiency and high luminance (US Patent No. 4,539,507). The organic EL device, as compared with inorganic ones, has characteristics that it can be driven by low voltage, has high luminance and in addition that a number of lights different in color can easily be obtained. Because of this, many trials are reported on device structures, organic fluorescent dyes and organic charge transport compounds [Japanese Journal of Applied Physics, Vol. 27, L269 (1988); Journal of Applied Physics, Vol. 65, p. 3610 (1989)].

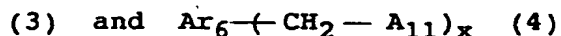
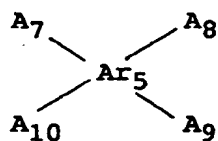
Organic EL devices so far reported are of high luminance, but have a problem that the life of the luminous device is short. The reason for this is said to be a change in the structure of the organic layer by generation of Joule's heat and deterioration of the layer caused by the change. Because of this, charge transport materials constituting a thermally stable organic layer have been demanded.

The present inventors have extensively studied to improve the heat resistance of the organic EL devices, and as a result have found that by using as the hole transport material particular aromatic amine compounds, for example, aromatic amine compounds of which the skeleton is an aromatic ring or triarylamine and which have been substituted with three or more amino groups at the aromatic nucleus (nuclei), or aromatic amine compounds of which the skeleton is an aromatic ring and which have been substituted with two or more dimethyl groups at the aromatic nucleus (nuclei), it is possible to form a uniform organic film, thereby improving the thermal stability and uniformity of light emission of the organic EL device. The present inventors thus attained to the present invention.

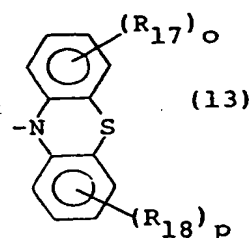
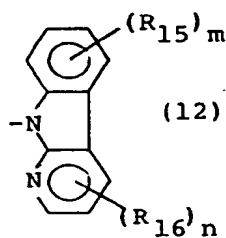
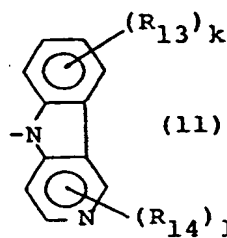
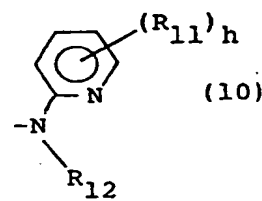
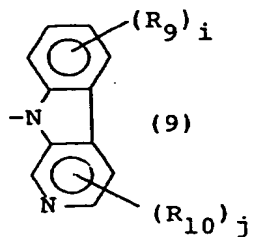
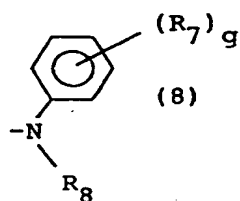
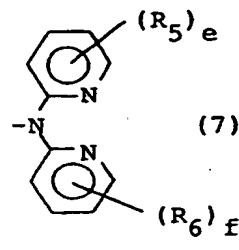
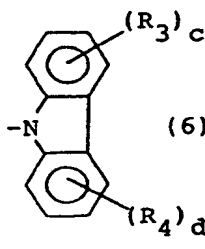
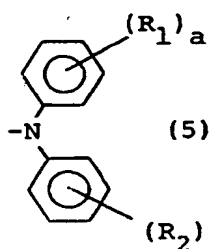
SUMMARY OF THE INVENTION

An object of the present invention is to provide an organic electroluminescence device having a luminous layer containing a luminous material and a hole transport material, or having a luminous layer containing a luminous material and a hole transport layer containing a hole transport material, between a pair of electrodes at least one of which is transparent or translucent, the above organic electroluminescence device being characterized in that the above hole transport material contains at least one aromatic amine compound selected from the group consisting of compounds represented by the formulae (1) to (4);





wherein each of Ar_1 , Ar_2 , Ar_3 , Ar_4 , Ar_5 and Ar_6 independently represents an aromatic hydrocarbon ring group having six or more carbon atoms or an aromatically heterocyclic compound group having four or more carbon atoms, x represents an integer of 2 or more, and each of A_1 , A_2 , A_3 , A_4 , A_5 , A_6 , A_7 , A_8 , A_9 , A_{10} and A_{11} independently represents a group selected from the following formulae (5) to (13) (plural A_i s may be the same or different);



wherein each of R_1 to R_7 , R_9 to R_{11} and R_{13} to R_{18} independently represents a member selected from the group consisting of C_1 - C_{12} alkyl and alkoxy groups, C_6 - C_{14} aryl and aryloxy groups, a nitro group and aromatically heterocyclic compound groups; when one benzene ring or pyridine ring has plural substituents, they are selected independently; each of R_8 and R_{12} independently represents a member selected from the group consisting of a hydrogen atom and C_1 - C_{12} alkyl groups; and a , b , c , d , e , f , g , h , i , j , k , l , m , n , o and p represent integers of $0 \leq a, b, g \leq 5$, $0 \leq c, d, e, f, h, i, k, m, o, p \leq 4$ and $0 \leq j, l, n \leq 3$.

PREFERRED EMBODIMENTS OF THE INVENTION

In the present invention, as luminous materials for organic EL devices, known ones can be used without particular limitation. For example, dyes such as naphthalene derivatives, anthracene derivatives, perylene der-

ivatives, polymethine dyes, xanthene dyes, coumarin dyes, cyanine dyes, etc., metal complexes of 8-hydroxy-quinoline and its derivatives, tetraphenylcyclopentadiene and its derivatives, tetraphenylbutadiene and its derivatives and known compounds described in US Patent No. 4,539,507 are mentioned.

Further, fluorescent conjugated polymers such as poly(p-phenylene vinylene), poly(2,5-dihexyloxy-p-phenylenevinylene), etc. having a short conjugated chain described in EP No. 0443861 also can be used.

Using these luminous materials, the luminous layer can be formed by properly selecting known methods, for example, vacuum deposition methods and coating methods such as spin coating, casting, dipping, bar coating and roll coating methods which use solutions of these luminous materials in solvents, according to the compounds used. When the luminous materials are not a high molecular compound, the vacuum deposition method is preferably used in carrying out fine control of film thickness.

The hole transport material used in the present invention is selected from the foregoing aromatic amine compounds represented by the formulae (1), (2), (3) and (4). In the aromatic amine compounds represented by the formulae (1), each of Ar_1 , Ar_2 and Ar_3 independently represents a group selected from the group consisting of aromatic hydrocarbon ring groups having six or more carbon atoms and aromatically heterocyclic compound groups having four or more carbon atoms. The groups Ar_1 , Ar_2 and Ar_3 may be different from one another, but in terms of ease of synthesis, two or more of them are preferably the same, and all of them are more preferably the same. The aromatic hydrocarbon ring groups having six or more carbon atoms that each of Ar_1 , Ar_2 and Ar_3 represents include those bonded at two positions of the skeleton such as benzene, biphenyl, naphthalene or anthracene. More specifically, there are given 1,4-phenylene, 1,3-phenylene, 1,2-phenylene, 4,4'-biphenylene, 1,4-naphthalenediyl, 2,6-naphthalenediyl and 9,10-anthracenediyl. The aromatically heterocyclic compound groups having four or more carbon atoms include those bonded at two positions of the skeleton such as thiophene, pyridine or quinoline. More specifically, there are given 2,5-thienylene, 2,3-pyridinediyl, 2,4-pyridinediyl, 2,5-pyridinediyl, 2,3-quinolinediyl, 2,6-quinolinediyl and the like. Among these groups described above, from the standpoints of synthesis being easy and high-melting temperature compounds being given, 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthalenediyl, 9,10-anthracenediyl, 2,5-thienylene, 2,5-pyridinediyl and 2,6-quinolinediyl are preferred, and 1,4-phenylene, 4,4'-biphenylene, 2,6-naphthalenediyl, 9,10-anthracenediyl and 2,5-pyridinediyl are more preferred.

In the aromatic amine compounds represented by the formulae (2) and (3), each of Ar_4 and Ar_5 represents aromatic hydrocarbon groups having six or more carbon atoms or aromatically heterocyclic compound groups having five or more carbon atoms. The aromatic hydrocarbon groups having six or more carbon atoms include 1,2,4-benzenetriyl, 1,3,5-benzenetriyl, 1,2,4-naphthalenetriyl, 1,3,5-naphthalenetriyl, 2,3,6-naphthalenetriyl, 3,5,4'-biphenyltriyl, 1,2,4,5-benzenetetrayl, 2,3,6,7-naphthalenetetrayl and 3,4,3',4'-biphenyltetrayl. The aromatically heterocyclic compound groups having five or more carbon atoms include 2,4,6-pyridinetriyl and 2,4,6-pyrimidinetriyl. Among these, more preferred ones are 1,3,5-benzenetriyl, 1,3,5-naphthalenetriyl, 2,3,6-naphthalenetriyl, 3,5,4'-biphenyltriyl, 2,4,6-pyridinetriyl and 2,3,6,7-naphthalenetetrayl. In the aromatic amine compounds represented by the formulae (1), (2) and (3), A_1 to A_{10} are a diphenylamino group, N-carbazolyl group, di-2-pyridylamino group, N-alkyl-N-phenylamino group, N-alkyl-N-2-pyridylamino group, N-pyrimido[3,4-b]indolyl group, N-pyrimido[4,5-b]indolyl group, N-pyrimido[2,3-b]indolyl group and N-phenothiazinyl group represented by the formulae (5) to (13), respectively, as described above and derivatives of these groups in which the nucleus of each groups has been substituted with a C_1 - C_{12} alkyl or alkoxy group, C_6 - C_{14} aryl or aryloxy group, nitro group or aromatically heterocyclic compound group. Each of R_8 and R_{12} independently represents a hydrogen atom or a C_1 - C_{12} alkyl group. Of these groups, a diphenylamino, N-carbazolyl and di-2-pyridylamino groups and their derivatives having a good film-forming property are preferred.

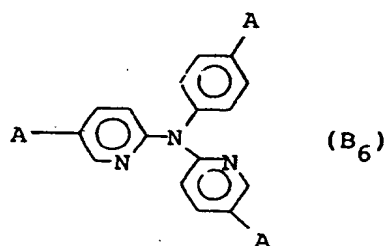
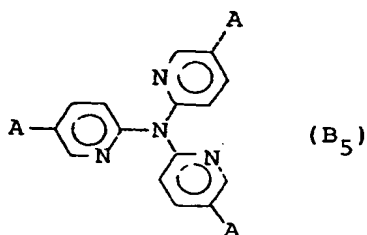
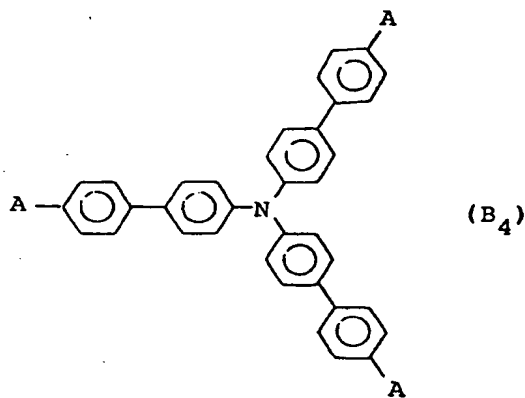
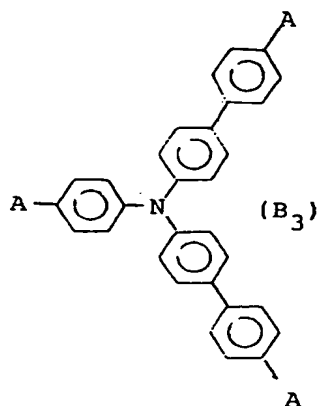
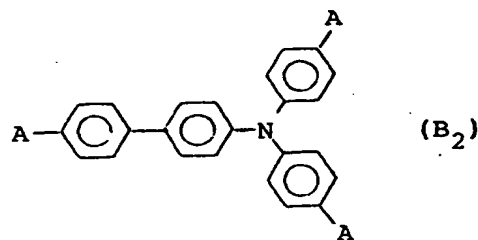
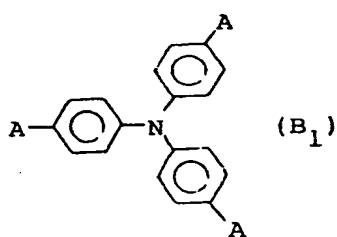
In the aromatic amine compounds represented by the formula (4), a group Ar_6 includes those having two or more $\{CH_2 - A_{11}\}$ groups at the skeleton of benzene, naphthalene, anthracene, biphenyl, fluorene, phenanthrene, quinoline or quinoxaline. Of these, benzene and biphenyl are preferred in terms of ease of reaction. The A_{11} group is selected from the groups represented by the foregoing formulae (5) to (13). Specifically, there are given a diphenylaminomethyl group, N-carbazolylmethyl group, di-2-pyridylaminomethyl group, N-alkyl-N-phenylaminomethyl group, N-alkyl-N-2-pyridylaminomethyl group, N-pyrimido[3,4-b]indolylmethyl group, N-pyrimido[4,5-b]indolylmethyl group, N-pyrimido[2,3-b]indolylmethyl group, N-phenothiazinylmethyl group and derivatives of these groups in which the aromatic ring (nucleus) of each group has been substituted with a C_1 - C_{12} alkyl or alkoxy group, C_6 - C_{14} aryl or aryloxy group, nitro group or aromatically heterocyclic compound group. Each of R_8 and R_{12} is independently selected from the group consisting of a hydrogen atom and a C_1 - C_{12} alkyl groups. Of these groups, those having a good film-forming property, i.e. a diphenylaminomethyl group and its derivatives, di-2-pyridylaminomethyl group and its derivatives and N-alkyl-N-phenylaminomethyl group and its derivatives are preferred. Hereupon, the above C_1 - C_{12} alkyl groups include for example a methyl, ethyl, butyl and octyl groups, etc., among which a methyl and ethyl groups are preferred. The C_1 - C_{12} alkoxy groups include a methoxy, ethoxy, butoxy and heptyloxy groups, etc., among which a methoxy and ethoxy groups are preferred.

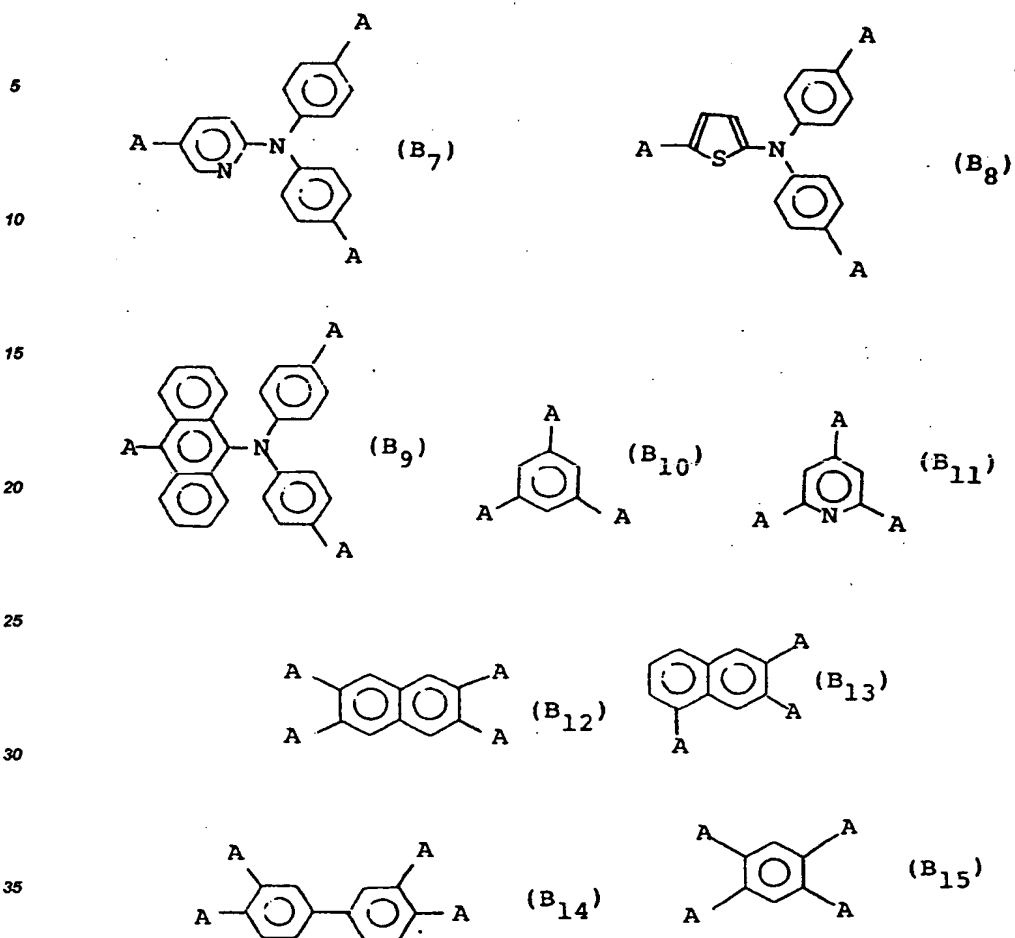
red. The aryl groups include a phenyl group, 4-C₁-C₆ alkylphenyl group (this means a phenyl group having a C₁-C₆ alkyl group at the 4-position), 4-C₁-C₆ alkoxyphenyl group (this means a phenyl group having a C₁-C₆ alkoxy group at the 4-position), 1-naphthyl group and 2-naphthyl group. The aryloxy groups include a phenoxy group, 4-C₁-C₆ alkylphenoxy group and 4-C₁-C₆ alkoxyphenoxy group. The aromatically heterocyclic compound group includes a 2-thienyl, 2-pyridyl, 3-pyridyl and 4-pyridyl groups. And, alkyl groups in the N-alkyl-N-phenylamino groups and N-alkyl-N-2-pyridylamino group represented by the formulae (8) and (10), respectively, represents C₁-C₁₂ alkyl groups, among which a methyl and ethyl groups are preferred.

In the above formula (4), there is no particular limitation to the number of aminomethyl substituents except that it is two or more. Usually, however, from the standpoint of ease of synthesis, the number of the aminomethyl substituents on the benzene ring is preferably 2 to 4, and that of the same substituents on the biphenyl group and condensed polycyclic compounds such as a naphthalene ring and an anthracene ring is preferably 2 to 6, particularly preferably 2 to 4.

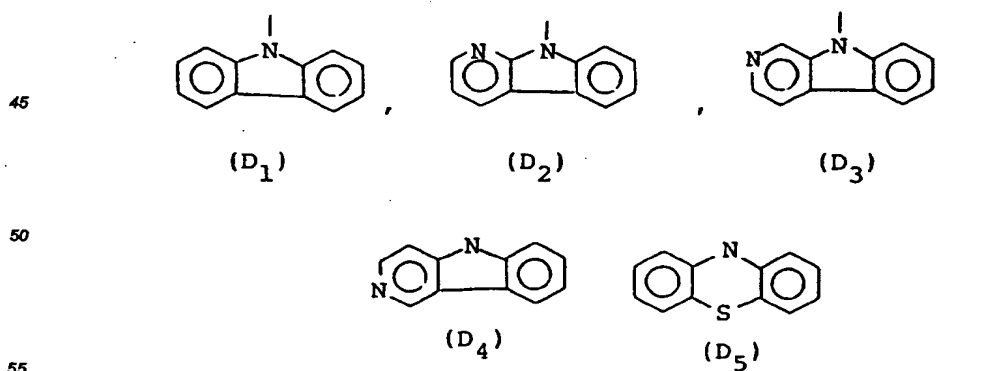
Specifically, there are given amine compounds described below:

Compounds represented by the formulae (B₁) to (B₁₆).

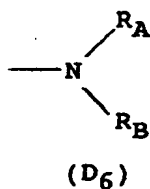




wherein A represents one of the groups represented by the formulae (D₁) to (D₅),



or a group represented by the formula (D₆),



10 wherein R_A or R_B are the same or different and are selected from, for example, methyl, ethyl, phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 4-tert-butylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 2-nitrophenyl, 4-(phenyl)phenyl, 4-(2-thienyl)phenyl, 4-(4'-methylphenyl)phenyl, 2-thienyl and 2-pyridyl, but R_A is neither methyl nor ethyl when R_B is methyl or ethyl. Specific examples of
15 combinations of R_A and R_B in the formula (D₆) are listed in Table 1.

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Table 1

	-R _A	-R _B
5	Phenyl	Phenyl
	2-Methylphenyl	2-Methylphenyl
10	3-Methylphenyl	3-Methylphenyl
	4-Methylphenyl	4-Methylphenyl
15	2-Ethylphenyl	2-Ethylphenyl
	3-Ethylphenyl	3-Ethylphenyl
	4-Ethylphenyl	4-Ethylphenyl
20	4-Tert-butylphenyl	4-Tert-butylphenyl
	4-Methoxyphenyl	4-Methoxyphenyl
25	4-Ethoxyphenyl	4-Ethoxyphenyl
	2-Nitrophenyl	2-Nitrophenyl
	4-(Phenyl)phenyl	4-(Phenyl)phenyl
30	4-(2-Thienyl)phenyl	4-(2-Thienyl)phenyl
	4-(4'-Methylphenyl)phenyl	4-(4'-Methylphenyl)phenyl
35	2-Thienyl	2-Thienyl
	Phenyl	Methyl
	Phenyl	Ethyl
40	Phenyl	2-Methylphenyl
	Phenyl	3-Methylphenyl
45	Phenyl	4-Methylphenyl
	Phenyl	2-Ethylphenyl

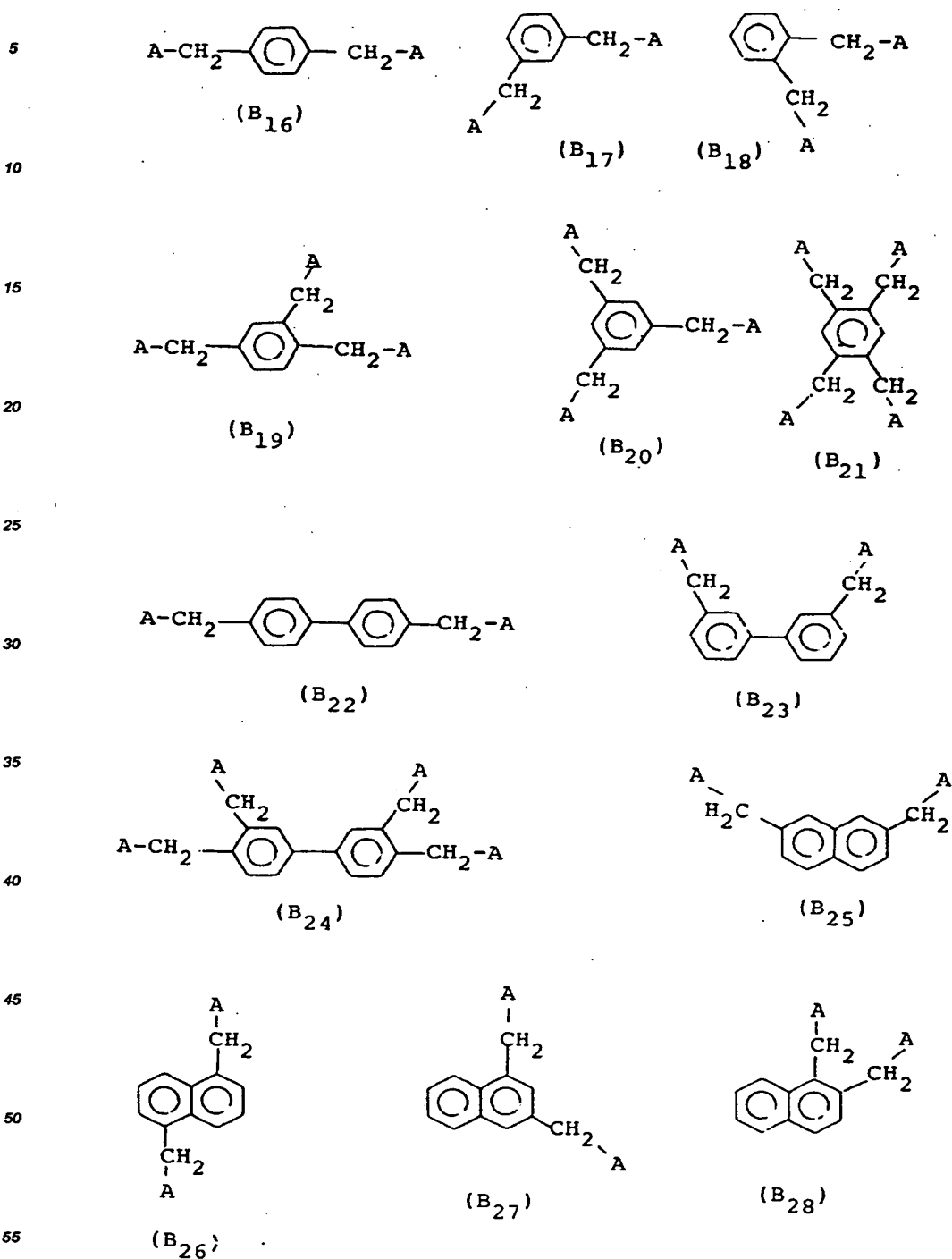
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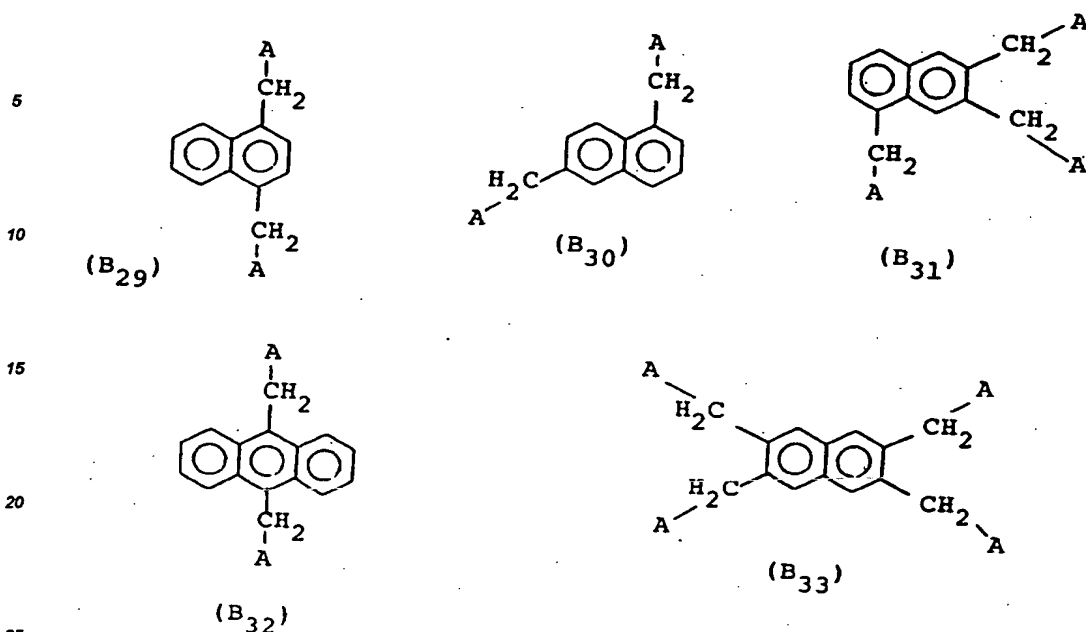
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	Phenyl	3-Ethylphenyl
	Phenyl	4-Ethylphenyl
5	Phenyl	4-Tert-butylphenyl
	Phenyl	4-Methoxyphenyl
10	Phenyl	4-Ethoxyphenyl
	Phenyl	2-Nitrophenyl
	Phenyl	2-Pyridyl
15	Phenyl	4-(Phenyl)phenyl
	Phenyl	4-(2-Thienyl)phenyl
20	Phenyl	4-(4'-Methylphenyl)phenyl
	Phenyl	2-Thienyl
	Methyl	2-Methylphenyl
25	Methyl	3-Methylphenyl
	Methyl	4-Methylphenyl
	Methyl	2-Ethylphenyl
30	Methyl	3-Ethylphenyl
	Methyl	4-Ethylphenyl
35	Methyl	4-Tert-butylphenyl
	Methyl	4-Methoxyphenyl
	Methyl	4-Ethoxyphenyl
40	Methyl	2-Nitrophenyl
	Methyl	2-Pyridyl
45	Methyl	4-(Phenyl)phenyl
	Methyl	4-(2-Thienyl)phenyl
	Methyl	4-(4'-Methylphenyl)phenyl
50	Methyl	2-Thienyl
	Ethyl	2-Methylphenyl
55	Ethyl	3-Methylphenyl

	Ethyl	4-Methylphenyl
5	Ethyl	2-Ethylphenyl
	Ethyl	3-Ethylphenyl
	Ethyl	4-Ethylphenyl
10	Ethyl	4-Tert-butylphenyl
	Ethyl	4-Methoxyphenyl
15	Ethyl	4-Ethoxyphenyl
	Ethyl	2-nitrophenyl
	Ethyl	2-Pyridyl
20	Ethyl	4-(Phenyl)phenyl
	Ethyl	4-(2-Thienyl)phenyl
25	Ethyl	4-(4'-methylphenyl)phenyl
	Ethyl	2-Thienyl
	2-Pyridyl	2-Pyridyl
30	2-Pyridyl	2-Methylphenyl
	2-Pyridyl	3-Methylphenyl
	2-Pyridyl	4-Methylphenyl
35	2-Pyridyl	2-Ethylphenyl
	2-Pyridyl	3-Ethylphenyl
40	2-Pyridyl	4-Ethylphenyl
	2-Pyridyl	4-Tert-butylphenyl
	2-Pyridyl	4-Methoxyphenyl
45	2-Pyridyl	4-Ethoxyphenyl
	2-Pyridyl	2-Nitrophenyl
50	2-Pyridyl	4-(Phenyl)phenyl
	2-Pyridyl	4-(2-Thienyl)phenyl
	2-Pyridyl	4-(4'-Methylphenyl)phenyl
55	2-Pyridyl	2-Thienyl

Further, there are given aromatic amines having a methyleneamine group represented by the formulae

(B₁₆) t (B₃₃).



wherein A represents one of the groups represented by the foregoing formulae (D₁) to (D₆) or the group represented by the foregoing formula (D₈), combination of R_A and R_B in (D₈) being specifically given in Table 1.

There is no particular limitation to a synthetic method for the aromatic amine compounds represented by the foregoing formulae (1), (2) and (3). Synthetic methods for these compounds will be shown below. Among the compounds represented by the formula (1), N,N,N-triphenylamine derivatives can be synthesized by adding KI, KIO₃ and acetic acid to triphenylamine to substitute iodine for hydrogen of the phenyl rings and reacting the resulting iodine-substituted product with the corresponding secondary amine compound and carbazole derivative. Among the compounds represented by the formula (2), 1,3,5-tris(diphenylamino)benzene derivatives can be synthesized by reacting 1,3,5-triodobenzene with the corresponding secondary amine compound and carbazole derivative. Among the compounds represented by the formula (3), 3,4,3',4'-tetra(diphenylamino)bi-phenyl derivatives can be synthesized by reacting 3,4,3',4'-tetraiodobiphenyl with the corresponding secondary amine compound and carbazole derivative. Other compounds can likewise be synthesized by making use of these reactions.

There is also no particular limitation to a synthetic method for the aromatic amine compounds represented by the formula (4), it being possible to make use of the known methods. for example, they can be synthesized by reacting an aromatic compound or its derivative having a halogenomethyl substituent at the predetermined position with the corresponding secondary amine compound or carbazole derivative.

When these compound are used as the hole transport layer of organic EL devices, it is desirable to purify them by reprecipitation, sublimation, etc. after synthesis because their purity affects the emission efficiency.

The hole transport layer containing the above aromatic amine compound can be formed by known methods, for example, vacuum deposition methods and coating methods such as spin coating, casting, dipping, bar coating and roll coating methods in which use solutions of the aromatic amine compounds are used. When the thin film of the layer is formed by the coating methods, it is desirable to apply heat-treatment at a temperature of 30° to 200°C, preferably 60° to 100°C under reduced pressure or in an inert gas atmosphere in order to remove the solvent. from the stand-point of carrying out fine control of the film thickness, to use the vacuum evaporation method is desirable. In producing the hole transport layer, the above aromatic amine compounds can be used alone or in mixture of two or more of them.

As far as the objects of the present invention are achieved, a mixture of the above hole transport aromatic amine compound and the known hole transport compound may be used for the hole transport layer of the present invention. In this case, in order to make the formed hole transport layer thermally stable, the content of the above aromatic amine compound is usually 1 wt.% or more, preferably 10 wt.% or more, more preferably 30 wt.% or more based on the known hole transport compound.

The known hole transport compound is not critical, but there are given for example triphenylamine derivatives, oxadiazole derivatives, pyrazoline derivatives, arylamine derivatives, stilben derivatives and the like. Specifically, there are given those described, for example, in US patent No. 4,539,507.

Since the thickness of the hole transport layer depends also upon the kind of the compounds used, it will suffice to properly determine the thickness taking that into account so as not to disturb sufficient development of the film-forming property and emission efficiency.

In the present invention, it is also included in the scope of the present invention to use a layer in which the hole transport aromatic amine compound has been dispersed in a known polymer. Such the polymers are not critical, but those which do not disturb the hole transport property to an extreme are preferred. For example, there are given poly(N-vinylcarbazole), polyaniline and its derivatives, polythiophene and its derivatives, poly(p-phenylenevinylene) and its derivatives, poly(2,5-thienylenevinylene) and its derivatives, polycarbonate, polysiloxane, vinyl polymers such as polymethyl acrylate, polymethyl methacrylate, polystyrene and polyvinyl chloride, and polyethersulfone and the like.

Hereupon, the above poly(N-vinylcarbazole), polyaniline and its derivatives, polythiophene and its derivatives, poly(p-phenylenevinylene) and its derivatives and poly(2,5-thienylenevinylene) and its derivatives act also as the hole transport compound.

The layer of mixture of the polymer and the aromatic amine compound can be formed by mixing the polymer and the compound in a solution state or molten state to disperse the compound in the polymer and then applying the above coating methods. In this case, there is no particular limitation to the amount of the aromatic amine compound to be mixed with the polymer, but it is usually 1 to 200 parts by weight, preferably 10 to 100 parts by weight based on 100 parts by weight of the polymer.

When the polymeric precursors of poly(p-phenylenevinylene) and its derivatives and poly(2,5-thienylenevinylene) and its derivatives are used, the precursor and the aromatic amine compound are mixed in a solution state, and the mixture is heat-treated at a temperature of 30° to 300°C, preferably 60° to 200°C in an inert gas atmosphere to convert the precursor to the polymer.

In the present invention, it is also possible to use a layer in which the hole transport aromatic amine compound and the luminous material have been dispersed in a known polymer.

The mixing ratio of the luminous material and hole transport material is not critical, but preferably it is in the range of 0.1:100 to 3:1 (weight ratio). The mixing ratio of the polymer and the sum of these materials also is not critical, but preferably it is in the range of 100:0.01 to 1:3 (weight ratio).

In this case, the polymer preferably used is those which are described above and have not a strong absorption to visible lights. Specifically, there are given poly(N-vinylcarbazole), polythiophene and its derivatives, poly(p-phenylenevinylene) and its derivatives, poly(2,5-thienylenevinylene) and its derivatives, polycarbonate, polymethyl acrylate, polymethyl methacrylate, polystyrene, polyvinyl chloride, polysiloxane and the like. For forming the mixture layer, the same coating methods as described above can be employed. These layers thus formed may be used alone, but if necessary, may be used in combination with layers of other hole transport or electron transport materials.

The structure of the organic EL device of the present invention will be illustrated below. The structure of the device, in addition to ones described hereinbefore, i.e. anode/hole transport layer/luminous layer/cathode (symbol "/" means laying layers one upon another) and anode/hole transport-luminous layer/cathode, may take a combined structure having an electro-conductive polymer layer (as a buffer layer) between the anode and hole transport layer and a combined structure having an electron transport layer between the luminous layer and cathode. Further, the structure of the device may also take a structure of anode/electro-conductive polymer layer/hole transport layer/luminous layer/electron transport layer/cathode. In some cases, it is also possible to form the respective hole transport layers of different hole transport materials and properly lay these layers one upon another, or properly lay the luminous layer(s) and hole transport layer(s) in two or more layers one upon another. Thus, modification is possible within the scope of the present invention.

A method for producing the organic EL device will be illustrated with reference to the structure of anode/hole transport layer/luminous layer/cathode.

A transparent or translucent electrode is formed on a transparent substrate such as glass, transparent plastics and the like, and used as an anode. A material for the electrode used includes electro-conductive metal oxide films, translucent metallic thin films and the like. Specifically, indium tin oxide (ITO), tin oxide (NESA), Au, Pt, Ag, Cu, etc. are used. For producing the electrode, methods such as vacuum deposition, sputtering, plating and the like are used.

Next, the foregoing hole transport layer is formed, and its thickness is 0.5 nm to 10 μ m, preferably 1 nm to 1 μ m. A thickness ranging from 2 to 200 nm is preferred in order to raise the luminance of emitted light by increasing current density.

Next, the luminous layer is formed on the hole transport layer, and its thickness needs to be such as on

as generating at least a pin holes. A too large thickness, however, is not preferred because it increases the resistance of the device to make a high driving voltage necessary. Consequently, the thickness of the luminous layer is 0.5 nm to 10 μm , preferably 1 nm to 1 μm , more preferably 5 to 200 nm.

This range of thickness is also preferred for the mixture layer of the hole transport material and luminous material.

Next, an electrode is formed on the luminous layer, as an electron-injecting cathode. Materials for the electrode are not critical, but materials of low work function are preferred. For example, Al, In, Mg, Mg/Ag alloy, Mg/In alloy, graphite thin film and the like are used. For producing the cathode, known methods such as vacuum deposition, sputtering and the like are used.

The organic EL device of the present invention can be produced by the method described above, but ones having other structures also can be produced by the similar method.

The aromatic amine compounds used as the hole transport material in the present invention have relatively high melting point and decomposition temperature, so that they are thermally stable.

The organic EL device with the hole transport material of the present invention, as compared with the conventional ones, has improved thermal stability and shows excellent emission characteristics, so that it can preferably be used in flat light sources as back light and display devices (e.g. flat panel display) and the like.

The present invention will be illustrated specifically with reference to the following examples, which are not however to be interpreted as limiting the invention thereto.

Example 1

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 4,4',4''-tris(diphenylamino)triphenylamine (hereinafter referred to as TDATA) in a thickness of 50 nm under a vacuum of 3×10^{-6} Torr. Thereafter, a luminous layer was formed thereon by vacuum-depositing tris(8-quinolinol)aluminum (hereinafter referred to as Alq₃) in a thickness of 80 nm, and then a cathode was further formed thereon by vacuum-depositing indium in a thickness of 600 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 3×10^{-6} Torr or less.

On applying a voltage of 25 V to this device, a current density of 208 mA/cm² and emission of green EL having a luminance of 210 cd/m² were observed. The luminance was directly proportional to the current density.

This device was put in a constant-temperature vessel, and a change in EL was observed while raising the temperature of the vessel. The device with TDATA as hole transport material continued to emit light even at a temperature over 100°C with its reduction in luminance being gently suppressed.

Example 2

On a glass substrate, to which an ITO film of 40 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing TDATA in a thickness of 40 nm under a vacuum of 3×10^{-6} Torr. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 40 nm, and then a cathode was further formed thereon by vacuum-depositing a Mg/Ag alloy (weight ratio, Mg : Ag = 10 : 1) in a thickness of 200 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 4×10^{-6} Torr or less. On applying a voltage of 11 V to this device, a current density of 295 mA/cm² and emission of green EL having a luminance of 820 cd/m² were observed. The luminance was directly proportional to the current density. On observing electroluminescence while heating this device in vacuum, emission of light having a luminance of 12 cd/m² was observed even at 130°C.

Example 3

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer in a thickness of 50 nm by spin coating of an N,N-dimethylformamide solution containing 0.5 wt.% of a mixture comprising the same weights of TDATA and polyaniline and then drying under reduced pressure. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 80 nm, and then a cathode was further formed thereon by vacuum-depositing indium in a thickness of 600 nm. Thus, the organic EL device was produced. Vacuum deposition was continuously carried out without breaking vacuum. All the pressures at the time of vacuum deposition were 3×10^{-6} Torr or less. On applying a voltage of 25 V to this device, a current density of 90 mA/cm² and emission of green EL having a luminance of 98 cd/m² were observed. The luminance was directly proportional to the current density. This device was put in a constant-temperature vessel, and a change in EL was observed while raising the temperature of the vessel. The

d vice with TDATA as charge transport material continued to emit light even at a temperature over 100°C with its reduction in luminance being gently suppressed.

Example 4

A chloroform solution containing 0.5 wt.% of a mixture comprising TDATA, Alq₃ and polycarbonate in a weight ratio of 1.75 : 1.25 : 7 was prepared. On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, a film was formed in a thickness of 170 nm by spin coating of the above solution and then drying under reduced pressure. Thereafter, a cathode was formed thereon by vacuum-depositing indium in a thickness of 600 nm to produce an organic EL device. Vacuum deposition was continuously carried out under reduced pressure without breaking vacuum. All the pressures at the time of vacuum deposition were 3×10^{-6} Torr or less. On applying a voltage of 52 V to this device, a current density of 31 mA/cm² and emission of green EL having a luminance of 2 cd/m² were observed. The luminance was directly proportional to the current density.

This device was put in a constant-temperature vessel, and a change in EL was observed while raising the temperature of the vessel. The device with TDATA as hole transport material continued to emit light even at a temperature over 100°C with its reduction in luminance being gently suppressed.

Example 5

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing TDATA in a thickness of 50 nm. Thereafter, a luminous layer was formed thereon by co-vacuum-depositing Alq₃ and 4-dicyanomethylene-6-(p-dimethylaminostyryl)-2-methyl-4H-pyran (hereinafter referred to as DCM) in a weight ratio of about 20 : 1 in a thickness of 40 nm, and then a cathode was further formed thereon by vacuum-depositing a Mg/Ag alloy (weight ratio, Mg : Ag = 10 : 1) in a thickness of 200 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 3×10^{-6} Torr or less.

On applying a voltage of 13 V to this device, a current density of 120 mA/cm² and emission of red EL having a luminance of 32 cd/m² were observed. The EL spectrum agreed with the fluorescent spectrum of DCM. The luminance was directly proportional to the current density.

This device was put in a constant-temperature vessel, and a change in EL was observed while raising the temperature of the vessel. The device with TDATA as hole transport material continued to emit light even at a temperature over 100°C with its reduction in luminance being gently suppressed.

Example 6

On a glass substrate, to which an ITO film of 40 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing TDATA in a thickness of 50 nm under a vacuum of 3×10^{-6} Torr. Thereafter, a luminous layer comprising 1,1,4,4-tetraphenyl-1,3-butadiene (hereinafter referred to as TPB), an electron transport layer comprising Alq₃ and a cathode comprising a Mg/Ag alloy (weight ratio, Mg : Ag = 10 : 1) were vacuum-deposited one upon another on the above hole transport layer in thickness of 20 nm, 40 nm and 200 nm, respectively. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 3×10^{-6} Torr or less.

On applying a voltage of 14.2 V to this device, a current density of 176 mA/cm² and emission of blue EL having a luminance of 89 cd/m² were observed. The EL spectrum agreed with the fluorescent spectrum of TPB. The luminance was directly proportional to the current density.

This device was put in a constant-temperature vessel, and a change in EL was observed while raising the temperature of the vessel. The device with TDATA as hole transport material continued to emit light even at a temperature over 100°C with its reduction in luminance being gently suppressed.

Example 7

On a glass substrate, to which an ITO film of 40 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 4,4',4''-tris(N-carbazolyl)triphenylamine in a thickness of 40 nm. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 40 nm, and then a cathode was further formed thereon by vacuum-depositing a Mg/Ag alloy (weight ratio, Mg : Ag = 10 : 1) in a thickness of 200 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 4×10^{-6} Torr or less.

On applying a voltage of 15 V to this device, a current density of 125 mA/cm² and emission of green EL having a luminance of 136 cd/m² were observed. The luminance was directly proportional to the current density.

This device was put in a constant-temperature vessel, and a change in EL was observed while raising the temperature of the vessel. The device with 4,4',4''-tris(N-carbazolyl)triphenylamine as hole transport material continued to emit light even at 130°C.

Example 8

On a glass substrate, to which an ITO film of 40 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 4,4',4''-bis(di-2-pyridylamino)triphenylamine in a thickness of 40 nm. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 40 nm, and then a cathode was further formed thereon by vacuum-depositing a Mg/Ag alloy (weight ratio, Mg : Ag = 10 : 1) in a thickness of 200 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 4 x 10⁻⁶ Torr or less.

On applying a voltage of 18 V to this device, a current density of 19.4 mA/cm² and emission of green EL having a luminance of 152 cd/m² were observed. The luminance was directly proportional to the current density.

On applying voltage to this device in vacuum with heating, emission of EL having a luminance of 44 cd/m² was observed even at 130°C.

Example 9

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 1,4-bis(N,N-diphenylaminomethyl)benzene in a thickness of 92 nm under a vacuum of 3 x 10⁻⁶ Torr. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 100 nm, and then a cathode was further formed thereon by vacuum-depositing indium in a thickness of 600 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 3 x 10⁻⁶ torr or less.

On applying a voltage of 30 V to this device, a current density of 79 mA/cm² and emission of green EL having a luminance of 42 cd/m² were observed. The luminance was directly proportional to the current density.

This device was heated to 80°C in vacuum, and the fluorescent spectrum of the heated device was measured with a fluorospectrophotometer (fluorospectrophotometer Model 850 produced by Hitachi Ltd.). However, a large change in the peak intensity of the fluorescent spectrum was not observed. The melting point of 1,4-bis(N,N-diphenylaminomethyl)benzene was measured with SSC5020 Thermal Analysis System (produced by Seiko Instruments Inc.) to find that it was 176°C.

Example 10

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 1,2,4,5-tetrakis(N-methyl-N-phenylaminomethyl)benzene in a thickness of 99 nm under a vacuum of 3 x 10⁻⁶ Torr. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 100 nm, and then a cathode was further formed thereon by vacuum-depositing indium in a thickness of 600 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 3 x 10⁻⁶ Torr or less.

On applying a voltage of 32 V to this device, a current density of 20 mA/cm² and emission of green EL having a luminance of 35 cd/m² were observed. The luminance was directly proportional to the current density.

On applying voltage to this device in vacuum with heating, emission of EL having a luminance of 5 cd/m² was observed even at 100°C. This device was heated to 80°C in vacuum in the same manner as in Example 9, but a large change in the fluorescent spectrum was not observed. The melting point of 1,2,4,5-tetrakis(N-methyl-N-phenylaminomethyl)benzene was measured in the same manner as in Example 9 to find that it was 199°C.

Example 11

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 4,4'-bis(N,N-diphenylaminomethyl)biphenyl in a thickness of 60 nm under a vacuum of 3 x 10⁻⁶ Torr. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 40 nm, and then a cathode was further formed thereon by vacuum-depositing indium in a thickness of 600 nm. Thus, the organic EL device was produced. All the pressures at the time of

vacuum deposition were 3×10^{-6} Torr or less.

On applying a voltage of 30 V to this device, a current density of 3.8 mA/cm² and emission of green EL having a luminance of 11.7 cd/m² were observed. The luminance was directly proportional to the current density.

On applying voltage to this device in vacuum with heating, emission of EL having a luminance of 5 cd/m² was observed even at 100°C. This device was heated to 80°C in vacuum in the same manner as in Example 9, but a large change in the fluorescent spectrum was not observed. The melting point of 4,4'-bis(N,N-diphenylaminomethyl)biphenyl was measured in the same manner as in Example 9 to find that it was 232°C. The above results show that this organic EL device has a good thermal stability.

10 Example 12

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 1,2,4-tris(N,N-diphenylaminomethyl)benzene in a thickness of 60 nm under a vacuum of 3×10^{-6} Torr. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 40 nm, and then a cathode was further formed thereon by vacuum-depositing indium in a thickness of 600 nm. Thus, the organic EL device was produced. All the pressures at the time of vacuum deposition were 3×10^{-6} Torr or less.

On applying a voltage of 43 V to this device, a current density of 1.2 mA/cm² and emission of green EL having a luminance of 25 cd/m² were observed. The luminance was directly proportional to the current density.

On applying voltage to this device in vacuum with heating, emission of EL having a luminance of 28 cd/m² was observed even at 80°C. This device was heated to 80°C in vacuum in the same manner as in Example 9, but a large change in the fluorescent spectrum was not observed.

25 Comparative Example 1

On a glass substrate, to which an ITO film of 20 nm in thickness was previously applied by sputtering, was formed a hole transport layer by vacuum-depositing 4,4'-bis[N-(3-methylphenyl)-N-phenylamino]biphenyl (hereinafter referred to as TPD) in a thickness of 50 nm under a vacuum of 3×10^{-6} Torr. Thereafter, a luminous layer was formed thereon by vacuum-depositing Alq₃ in a thickness of 80 nm, and then a cathode was further formed thereon by vacuum-depositing indium in a thickness of 600 nm. Thus, the organic EL device was produced. Vacuum deposition on every layer was continuously carried out under reduced pressure without breaking vacuum. All the pressures at the time of vacuum deposition were 3×10^{-6} Torr or less.

On applying voltage to this device in vacuum with heating, emission of EL became very weak at 80°C, and there was no emission at all at 100°C.

After this device was heated to 60°C in vacuum, its fluorescent spectrum was measured in the same manner as in Example 9 to find that the intensity of the spectrum showed a great change as compared with that of the fluorescent spectrum at room temperature. The melting point of TPD was measured in the same manner as in Example 9 to find that it was 169°C.

40 Comparative Example 2

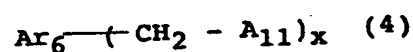
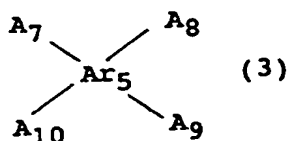
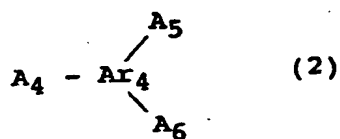
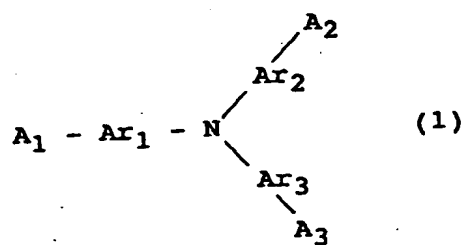
The organic EL device was produced in the same manner as in Example 8 except that TPD was used in place of 4,4'-4"-tris(di-2-pyridylamino)triphenylamine.

On applying voltage to this device in vacuum with heating, emission of EL became very weak at 80°C, and there was no emission at all at 100°C.

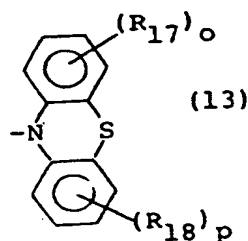
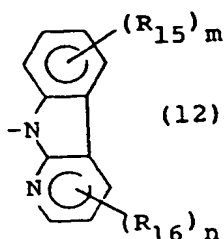
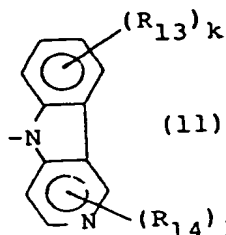
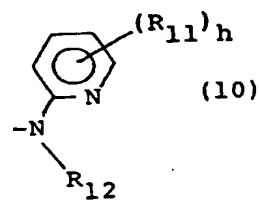
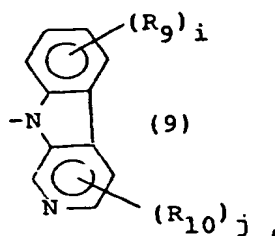
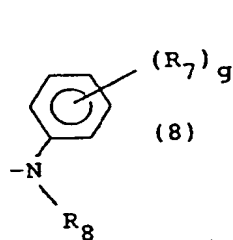
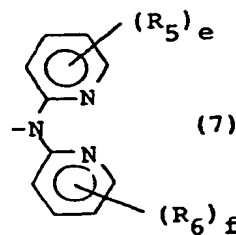
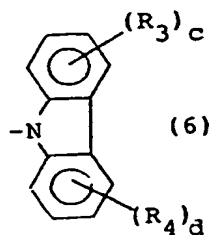
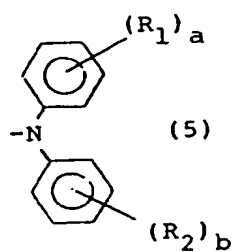
After this device was heated to 60°C in vacuum, its fluorescent spectrum was measured in the same manner as in Example 9 to find that the strength of the spectrum showed a great change as compared with that of the fluorescent spectrum at room temperature.

50 Claims

1. An organic electroluminescence device comprising either
 - (a) a luminous layer containing a luminous material and an hole transport material, or
 - (b) a luminous layer containing a luminous material and a hole transport layer containing a hole transport material,
 between a pair of electrodes at least one of which is transparent or translucent, wherein the hole transport material contains an aromatic amine of formula (1), (2), (3) or (4):

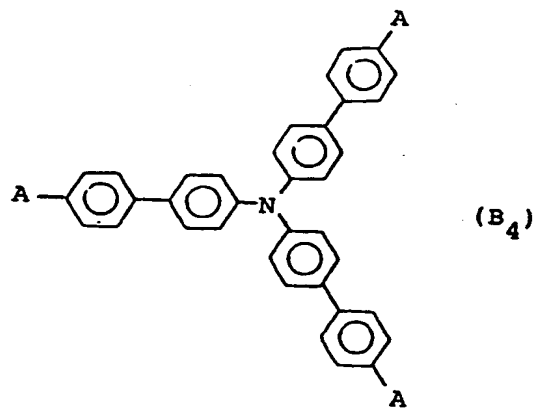
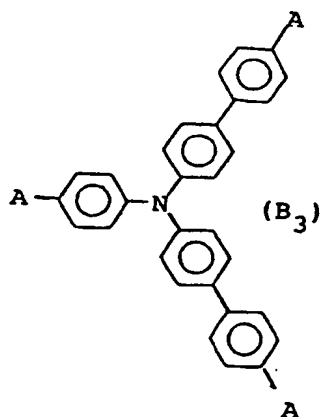
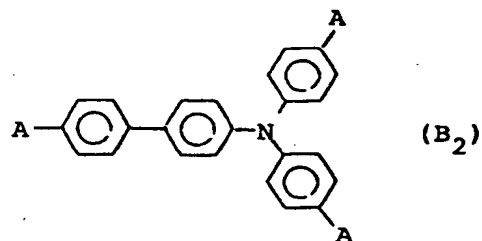
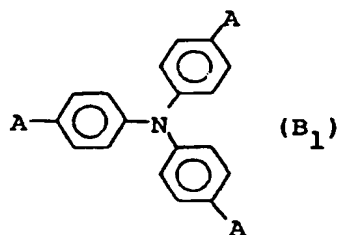


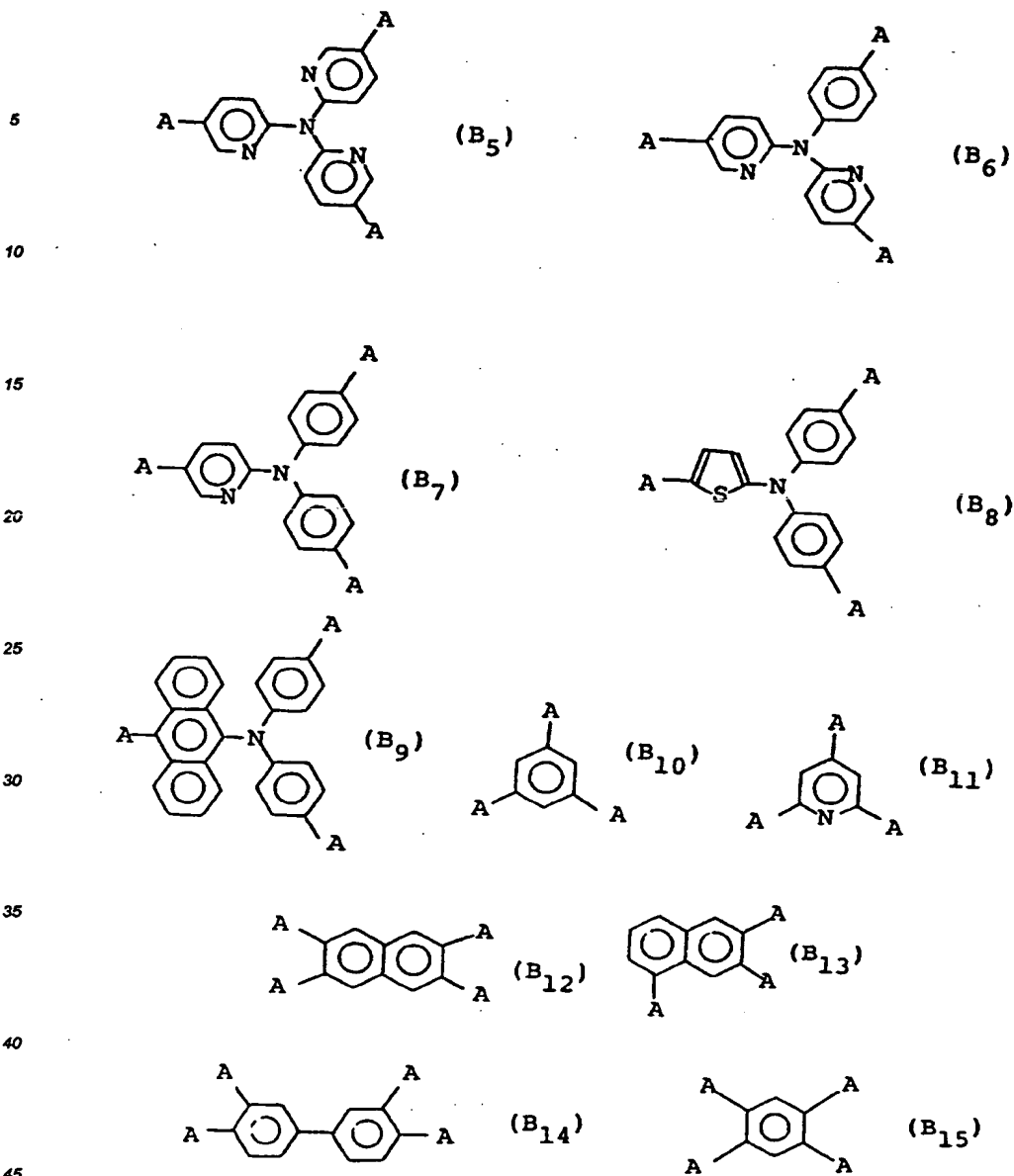
wherein the groups Ar^1 , Ar^2 , Ar^3 , Ar^4 , Ar^5 and Ar^6 are independently selected from aromatic hydrocarbon groups having six or more carbon atoms and aromatic heterocyclic groups having four or more carbon atoms, x in formula (4) is an integer of 2 or more and the groups $(CH_2 - A_{11})$ are the same or different, and the groups A^1 , A^2 , A^3 , A^4 , A^5 , A^6 , A^7 , A^8 , A^9 , A^{10} and A^{11} , are independently selected from the groups of formulae (5) to (13):



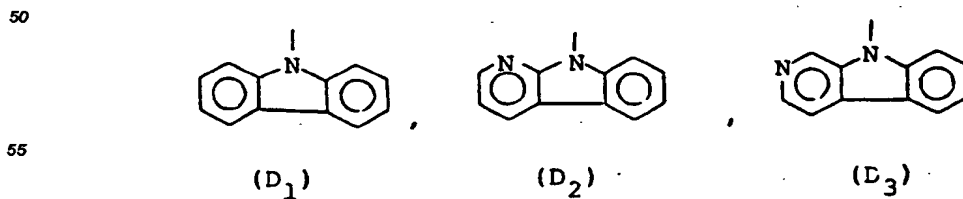
wherein each of R^1 to R^7 , R^9 to R^{11} and R^{13} to R^{18} is independently selected from C_1 - C_{12} alkyl and alkoxy groups, C_6 - C_{14} aryl and aryloxy groups, nitro and aromatic heterocyclic groups, R^8 and R^{12} are each hydrogen or C_1 - C_{12} alkyl and $a, b, c, d, e, f, g, h, i, j, k, l, m, n, o$ and p are integers of $0 \leq a, b, g \leq 5$, $0 \leq c, d, e, f, h, i, k, m, o, p \leq 4$ and $0 \leq j, l, n \leq 3$.

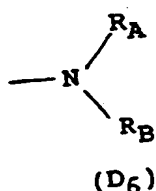
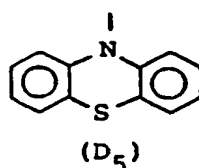
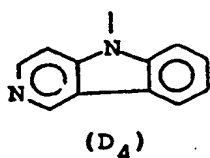
2. A device according to claim 1 comprising a luminous layer and a hole transport layer wherein the hole transport layer is composed of a mixture of the aromatic amine compound and a polymer.
3. A device according to claim 2, wherein the hole transport layer comprises 1 to 200 parts by weight of the aromatic amine compound per 100 parts by weight of the polymer.
4. A device according to claim 1 (a) comprising a luminous material and a hole transport material dispersed in a polymer.
5. A device according to claim 4 wherein the weight ratio of the luminous material to the hole transport material in the luminous layer is in the range of 0.1:100 to 3:1.
6. A device according to claim 4 or claim 5 wherein the weight ratio of the polymer to the sum of the luminous material and hole transport material is in the range of 100:0.01 to 1:3.
7. A device according to any one of claims 2 to 6, wherein the polymer is selected from polymers of N-vinylcarbazole, aniline and its derivatives, thiophene and its derivatives and p-phenylenevinylene and its derivatives, polycarbonates, polysiloxanes, vinyl polymers and polyethersulfones.
8. A device according to any one of claims 1 to 7 wherein the hole transport material is selected from the compounds of formulae (B¹) to (B¹⁵):





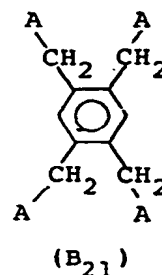
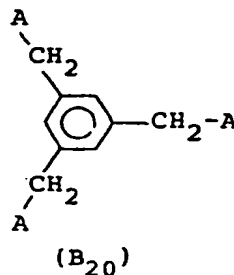
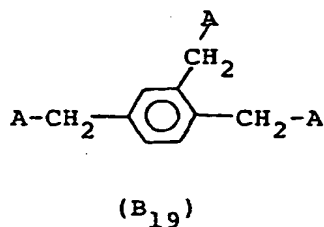
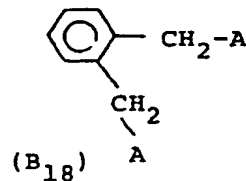
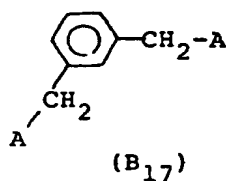
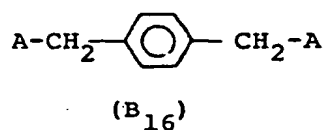
wherein in each case the groups A are the same or different and each group A is selected from the groups of formulae (D¹) to (D⁶):



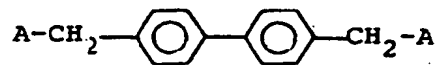


wherein R^A and R^B are the same or different and each is methyl, ethyl, phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 4-tert-butylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 2-nitrophenyl, 4-(phenyl)phenyl, 4-(2-thienyl)phenyl, 4-(4'-methylphenyl)phenyl, 2-thienyl or 2-pyridyl provided that R^A is not methyl or ethyl when R^B is methyl or ethyl.

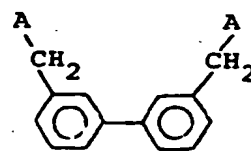
9. A device according to claim 8 wherein the hole transport material is a compound of formula (B¹) wherein A is a group selected from the groups of formulae (D¹) to (D⁵) and groups of formula (D⁶) wherein R^A is phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 4-tert-butylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 2-nitrophenyl, 4-(phenyl)phenyl, 4-(2-thienyl)phenyl, 4-(4'-methylphenyl)phenyl, 2-thienyl or 2-pyridyl, and R^B is 4-tert-butylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 2-nitrophenyl, 4-(phenyl)phenyl, 4-(2-thienyl)phenyl, 4-(4'-methylphenyl)phenyl, 2-thienyl or 2-pyridyl.
10. A device according to any one of claims 1 to 7 wherein the hole transport material is selected from the compounds of formulae (B¹⁶) to (B³³):



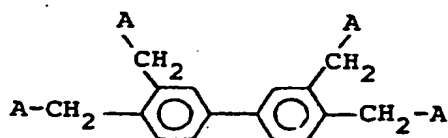
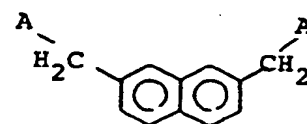
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(B₂₂)

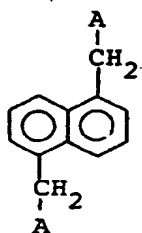
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(B₂₃)

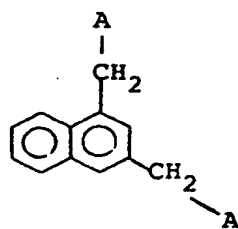
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(B₂₄)(B₂₅)

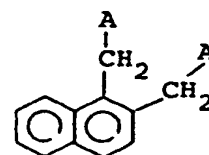
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(B₂₆)

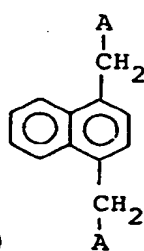
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(B₂₇)

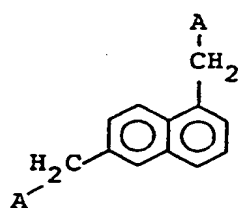
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(B₂₈)

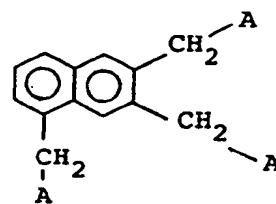
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(B₂₉)

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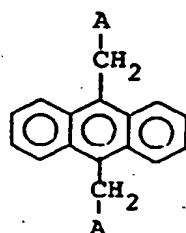
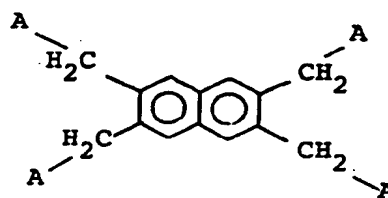
(B₃₀)

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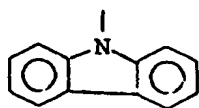
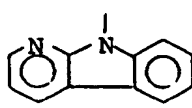
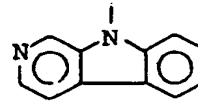
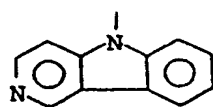
(B₃₁)

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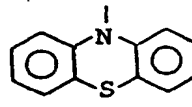
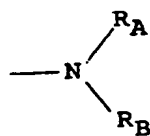
55

(B₃₂)(B₃₃)

wherein in each case the groups A are the same or different and each group A is selected from the groups of formulae (D¹) to (D⁶).

(D₁)(D₂)(D₃)(D₄)

and

(D₅)(D₆)

wherein R^A or R^B are the same or different and each is methyl, ethyl, phenyl, 2-methylphenyl, 3-methylphenyl, 4-methylphenyl, 2-ethylphenyl, 3-ethylphenyl, 4-ethylphenyl, 4-tert-butylphenyl, 4-methoxyphenyl, 4-ethoxyphenyl, 2-nitrophenyl, 4-(phenyl)-phenyl, 4-(2-thienyl)phenyl, 4-(4'-methylphenyl)phenyl, 2-thienyl or 2-pyridyl provided R^A is not methyl or ethyl when R^B is methyl or ethyl.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number

DOCUMENTS CONSIDERED TO BE RELEVANT			EP 92305184.1
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 15, no. 353, September 06, 1991 THE PATENT OFFICE JAPANESE GOVERNMENT page 7 C 865 * Kokai-no. 3-137 186 (ASAHI) *	1, 2	H 05 B 33/14 H 05 B 33/28
A	PATENT ABSTRACTS OF JAPAN, unexamined applications, C field, vol. 15, no. 302, August 02, 1991 THE PATENT OFFICE JAPANESE GOVERNMENT page 50 C 855 * Kokai-no. 3-111 484 (MINOLTA) *	1	
D, A	US - A - 4 539 507 (VAN SLYKE) * Column 9, lines 49-62; claims 1, 7 *	1	TECHNICAL FIELDS SEARCHED (Int. CL.5) H 05 B 33/00
A	EP - A - 0 399 508 (MITSUBISHI) * Claims 1, 8 *	1	
A	US - A - 4 769 292 (TANG) * Column 44, lines 49-68; claims 1, 4, 19 *	1	
A	US - A - 4 720 432 (VAN SLYKE) * Column 4, lines 36-47; example 1; claims 1, 17; fig. 1 *	1	
The present search report has been drawn up for all claims			
Place of search VIENNA		Date of completion of the search 31-07-1992	Examiner TSILIDIS
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

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